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# Flame-photometric Determination of Strontium in Natural Water

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**GEOLOGICAL SURVEY WATER-SUPPLY PAPER 1496-C**

*Prepared on behalf of the U.S. Atomic  
Energy Commission and published with  
the permission of the Commission*



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BY C. ALBERT HERR

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**UNITED STATES DEPARTMENT OF THE INTERIOR**

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**GEOLOGICAL SURVEY**

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## CONTENTS

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	Page
Abstract.....	33
Introduction.....	33
Flame photometry.....	34
Interferences in flame photometry.....	34
Analytical procedure.....	42
Flame-photometric method.....	42
Ion-exchange method.....	43
Results and discussion.....	51
References cited.....	52

## ILLUSTRATIONS

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FIGURE 3. Effect of ions on strontium emission.....	38
4. Effect of pH on strontium emission.....	41
5. Typical calibration curve.....	44
6. Elution curve for strontium, group 1 eluates.....	46
7. Elution curve for strontium, group 2 eluates.....	47
8. Elution curve for strontium and calcium.....	48
9. Ion-exchange column.....	50

## TABLES

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TABLE 1. Band-width interference of various ions.....	37
2. Effect of various elements on the emission of the 460.7 $m\mu$ strontium line.....	39
3. Comparison of results obtained by the flame-photometric, ion-exchange flame-photometric, and spectrographic methods....	51
4. Recovery of strontium added to tap water. Analysis by the flame-photometric procedure.....	51
5. Recovery of strontium added to a synthetic water. Analysis by the ion-exchange flame-photometric method.....	52

## CHEMISTRY OF STRONTIUM IN NATURAL WATER

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### FLAME-PHOTOMETRIC DETERMINATION OF STRONTIUM IN NATURAL WATER

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By C. ALBERT HERR

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#### ABSTRACT

The strontium content of natural waters is rarely over 10 ppm and most natural waters have concentrations of 1.0 ppm or less. Gravimetric and volumetric methods are unsatisfactory for the determination of strontium in this concentration range. Flame-photometric methods, however, have the required sensitivity to determine strontium in the 0.02 to 10 ppm concentration range.

A study was made of interferences caused by common ions present in natural water on the determination of strontium. The flame-photometric method is capable of detecting as little as 0.2 ppm strontium with an accuracy of  $\pm 10$  percent. The method is applicable to waters containing 0.2 to 10 ppm of strontium. Higher concentrations require dilution.

A method for concentrating strontium in waters containing less than 0.2 ppm by means of ion-exchange chromatography is presented. With this method a tenfold concentration is effected which permits strontium to be determined at concentrations as low as 0.02 ppm within an accuracy of  $\pm 10$  percent.

#### INTRODUCTION

This study was undertaken to develop a rapid, sensitive, and accurate method for the determination of naturally occurring strontium in water. Strontium is present in all natural water at concentrations, generally ranging from 0.01 to 40 ppm (parts per million).

Although gravimetric and volumetric methods are satisfactory for the determination of large amounts of strontium, these methods are time consuming and lack the sensitivity required to determine strontium in amounts less than 10 ppm. Flame-photometric methods, however, are rapid, require little or no pretreatment of samples, and are especially recommended for the determination of strontium in the presence of the other alkaline-earth metals.

Two methods for the determination of strontium in natural water are presented in this report. The flame-photometric method has been modified from the method described by Skougstad (1957). It is rapid, requires little pretreatment of the sample, and is capable of

detecting as little as 0.2 ppm strontium. An accuracy within  $\pm 10$  percent is obtainable over the range of 0.2 to 10 ppm.

Analyses of a representative group of samples of surface and ground water from throughout the United States show that the strontium content of water in a significant number of samples is less than 0.2 ppm (Skougstad and Horr, 1960). Because the flame-photometric method is not sensitive for less than 0.2 ppm of strontium, it is necessary to increase the strontium concentration tenfold to determine strontium in the 0.02 to 0.2 ppm concentration range. The use of ion-exchange chromatography as an adjunct to the flame-photometric method is described. With this method as little as 0.02 ppm of strontium may be determined within an accuracy of  $\pm 10$  percent.

This work was done on behalf of the U.S. Atomic Energy Commission.

### FLAME PHOTOMETRY

Although the flame had been used as early as 1848 as a source of excitation for the production of emission spectra, Kirchhoff and Bunsen (1860) were the first to use it for qualitative analysis. With few minor exceptions, the use of the flame as an excitation source in spectroscopy was abandoned in favor of electric-arc and spark excitation sources until 1929, when Lundegårdh published his classic work on flame photometry. This work firmly established flame spectrophotometry as a modern analytical tool. In recent years, the availability of commercially made flame spectrophotometers with improved flame sources, optical systems, and photodetecting systems has extended the scope of flame photometry for the determination of approximately 50 elements.

In the analysis of water, the flame photometer is indispensable for the determination of sodium, potassium, and lithium. It may be used for the determination of alkaline-earth and other metals in natural water, such as cesium (detection limit 0.1 ppm), rubidium (0.01 ppm), copper (0.01 ppm), manganese (0.01 ppm), and others. It is especially recommended for the determination of milligram amounts of strontium in the presence of calcium and magnesium.

### INTERFERENCES IN FLAME PHOTOMETRY

Quantitative flame photometry is subject to interferences caused by variation in the instrumental system and variations in composition and physical properties of the analysis solution. Instrumental interferences may be minimized or eliminated by proper adjustment of such variables as wavelength, slit width, sensitivity of spectrometer and phototube, and ratio of fuel gas to supporting gas.

Interference caused by variations in the composition of the analysis solution can be grouped into three major types. Band-width inter-

ference occurs when the analysis element and an interfering element radiate at nearly the same wavelength and the two are read together. Commonly band-width interference is eliminated or reduced by using as narrow a slit width as possible. For some analyses it is possible to select another wavelength that will be free of band-width interference.

Radiation interferences are the result of interatomic or intermolecular processes between the analysis element and an interfering element in the flame. Studies by Huldtt (1944), Taylor and Paige (1955), Chow and Thompson (1955), and others have shown that radiation interference caused by anions will generally depress the emission of the analysis element. A notable exception to this is the perchlorate ion. Radiation interference caused by cations may either enhance or depress the emission of the analysis element.

Radiation interferences commonly will reach a plateau where further increase in the concentration of the interfering element has little additional effect on the emission of the analysis element. Addition of excess interferant as a radiation buffer to both standard and sample solutions will affect each equally and thus mask the effects of interference. West and others (1950) and Skougstad (1957) describe methods that use radiation buffers to compensate for radiation interferences.

Background interference is the result of continuous emission from the flame and solvent and is superimposed on the analytical emission causing an apparent increase in the concentration of the analysis element. Vallee (1957, p. 252) states

\* \* \* the background observed is a consequence of the molecular events when a solution is sprayed into a flame. First, there is dehydration and formation of crystals which must be vaporized before excitation of the atoms may take place. If these crystals have a high boiling point, vaporization does not occur, and a proportion of this material will then serve as a source of "black-body" radiation, accounting for the observed background.

A correction for background interference may be made by subtracting the emission intensity measured at a wavelength close to the wavelength of the analysis element from the emission intensity of this element. This correction will apply only if the magnitude of the background emission is the same at both wavelengths. It is also possible to use the average value of the background emission, measured at wavelengths above and below the analytical wavelength, as a correction factor.

The magnitude of background emission varies with the square of the slit width, whereas response to an emission line varies with the first power; thus, the background may be reduced by using a narrower slit. The use of hydrogen as a fuel also will reduce background emis-

sion (Burriel-Martí and Ramírez-Muñoz, 1957, p. 42). Ideally, the background emission should be no greater than 10 to 20 percent of the total emission.

All interference errors can be eliminated by comparing standards and samples of identical composition and concentration. Thus, standard and sample are subject to the same conditions in the flame. Dilution of the sample will eliminate or reduce radiation interference, but may decrease the concentration of the analysis element below its detection limit.

Because natural waters vary widely in content of dissolved materials, a study was made to determine the nature and magnitude of interferences caused by the common cations and anions on the emission intensity of strontium.

Stock solutions containing 1,000 ppm of aluminum, ammonium, calcium, iron (ferric), magnesium, potassium, and sodium were prepared from their chloride salts. The sulfate and phosphate stock solutions were prepared from their ammonium salts. The silica solution was prepared by the hydrolysis of tetraethyl orthosilicate. A series of standards containing 10, 20, 30, 40, 50, 100, 200, and 500 ppm each of the cations was prepared from the stock solutions. A similar series of cation and anion standards containing 10 ppm of strontium in each was also prepared.

A Beckman DU quartz spectrophotometer equipped with a photomultiplier and flame-photometer attachment was used for all measurements. The atomizer burner was operated at an oxygen pressure of 11.0 psi and acetylene pressure of 5.5 psi. The 460.7-m $\mu$  atomic strontium line was chosen for the measurements, because of its sensitivity. Corrections for background emission were made by subtracting the emission intensity measured at 458 m $\mu$  from the intensity at 460.7 m $\mu$ .

For the determination of band-width interferences, the flame photometer was adjusted to 100-percent transmission for 10 ppm strontium. Solutions containing 10, 20, 30, 40, 50, 100, 200, and 500 ppm of aluminum, calcium, iron, magnesium, potassium, and sodium were then atomized in the flame and the emission intensity readings taken at 460.7 m $\mu$  and 458 m $\mu$ . As indicated in table 1, aluminum, iron, magnesium, potassium, and sodium gave no net emission intensity at 460.7 m $\mu$  and hence produced no band-width interference. Calcium produces band-width interference with concentrations above 50 ppm and has a net emission intensity at 460.7 m $\mu$ .

Radiation interferences were studied by aspirating solutions containing 10.0 ppm of strontium and varying amounts of individual cations and anions and measuring the resulting emission intensity at 460.7 m $\mu$ . No attempt was made to study the effect of mixtures of

TABLE 1.—*Band-width interference of various ions*

Constituent	Concentration (ppm)	Emission intensity at 460.7 m $\mu$	Emission intensity at 458 m $\mu$	Net emission intensity	Constituent	Concentration (ppm)	Emission intensity at 460.7 m $\mu$	Emission intensity at 458 m $\mu$	Net emission intensity
Aluminum---	10	49	49	0	Magnesium--	10	50	50	0
	20	49	49	0		20	50	50	0
	30	49	49	0		30	50	50	0
	40	49	49	0		40	50	50	0
	50	49	49	0		50	50	50	0
	100	49	49	0		100	50	50	0
	200	49	49	0		200	50	50	0
	500	49	49	0		500	50	50	0
Calcium-----	10	60	60	0	Potassium---	10	49	49	0
	20	60	60	0		20	49	49	0
	30	60	60	0		30	49	49	0
	40	60	60	0		40	49	49	0
	50	60	60	0		50	49	49	0
	100	62	60	2		100	49	49	0
	200	66	62	4		200	49	49	0
	500	66	62	4		500	49	49	0
Iron (ferric)--	10	50	50	0	Sodium-----	10	49	49	0
	20	50	50	0		20	49	49	0
	30	50	50	0		30	49	49	0
	40	50	50	0		40	49	49	0
	50	50	50	0		50	49	49	0
	100	50	50	0		100	49	49	0
	200	50	50	0		200	49	49	0
	500	59	59	0		500	53	53	0

cations and anions or of ions not commonly found in natural waters. The results obtained, shown in table 2 and figure 3, are expressed as the ratio:

$$\frac{\text{Emission intensity of Sr+ added ion}}{\text{Emission intensity of Sr alone}} \times 100$$

Thus, ratios greater than 100 indicate enhancement of strontium emission and ratios less than 100 indicate depression of strontium emission.

Sodium and potassium enhance the strontium emission. The enhancement effects are nearly identical for equal amounts of sodium or potassium, but are not proportional to the quantity of ion present. The enhancement by sodium or potassium may be due in part to the suppression of the ionization of strontium (ionization reduces the intensity of the 460.7-m $\mu$  strontium line) in the flame by the more easily ionized alkali metals. Wilson (1931), however, has shown that ions are rarely produced at the temperatures attained in the flame. Enhancement of the strontium emission is probably the result of energy transfer from excited sodium or potassium atoms present in the flame.

Calcium also enhances strontium emission. However, the effect was constant at calcium-to-strontium concentration ratios of 3 to 1 and greater. Mitchell and Robertson (1936) suggested that the enhancement is the result of an energy transfer. Huldtt (1944) concluded that a shift in ionization equilibrium causes the increase in the emission intensity of strontium with added calcium.

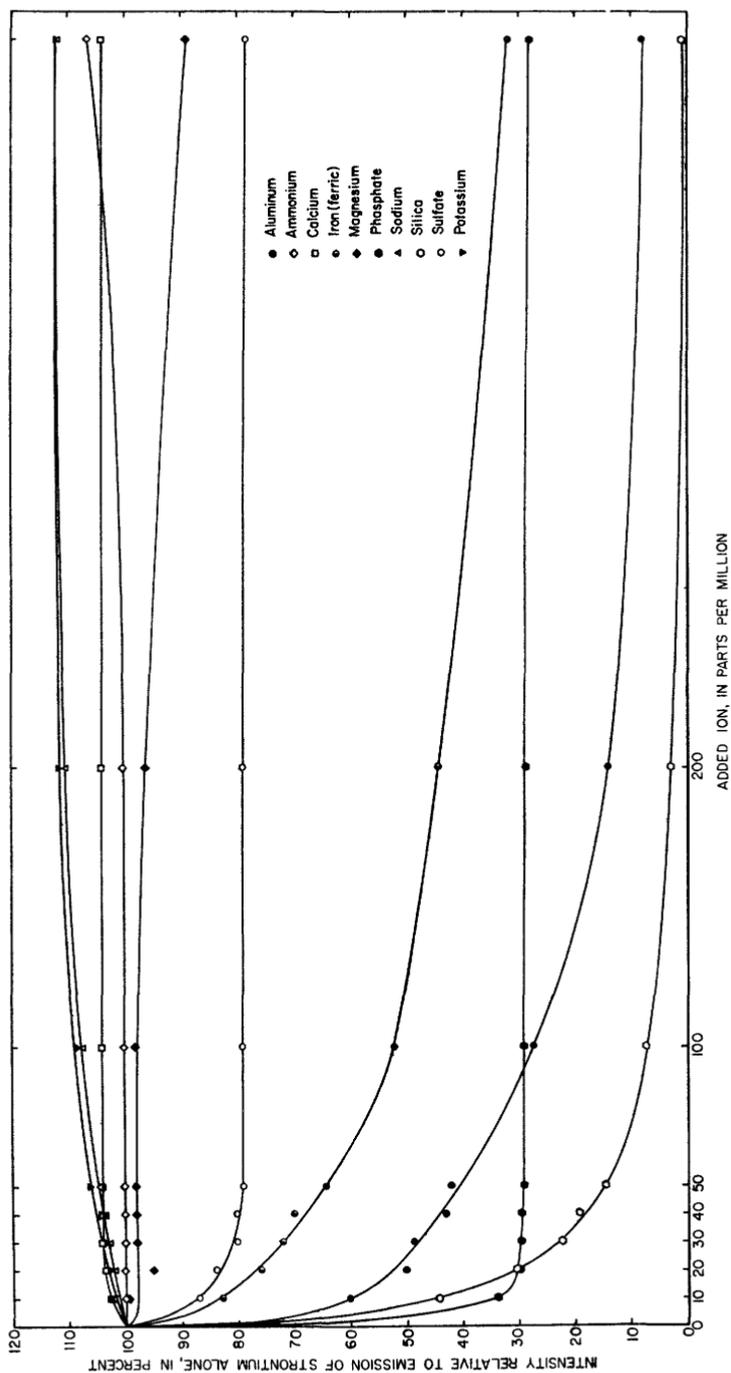


FIGURE 3.—Effect of various ions on the emission of the 460,7-m $\mu$  strontium line. Strontium content 10.0 ppm.

TABLE 2.—*Effect of various elements on the emission of the 460.7-m $\mu$  strontium line*  
 [Strontium=10 ppm]

Constituent	Concentration (ppm)	Emission ratio $\frac{\text{Sr}+\text{M ion}}{\text{Sr}} \times 100$	Constituent	Concentration (ppm)	Emission ratio $\frac{\text{Sr}+\text{M ion}}{\text{Sr}} \times 100$
Sodium.....	0	100.0	Calcium.....	0	100.0
	10	100.0		10	102.2
	20	102.8		20	103.6
	30	102.8		30	104.0
	40	104.0		40	104.0
	50	105.8		50	104.0
	100	108.0		100	104.0
	200	110.4		200	104.0
	500	112.0		500	104.2
Potassium.....	0	100.0	Magnesium.....	0	100.0
	10	102.0		10	100.0
	20	102.0		20	95.0
	30	103.6		30	98.0
	40	104.4		40	98.0
	50	106.0		50	98.0
	100	108.4		100	98.0
	200	111.8		200	96.0
	500	112.0		500	89.0
Iron.....	0	100.0	Aluminum.....	0	100.0
	10	83.0		10	60.2
	20	76.0		20	50.2
	30	76.0		30	48.8
	40	70.0		40	43.0
	50	64.4		50	42.0
	100	52.2		100	27.2
	200	44.0		200	14.0
	500	31.8		500	8.0
Phosphate.....	0	100.0	Sulfate.....	0	100.0
	10	87.0		10	33.8
	20	84.0		20	30.0
	30	80.2		30	29.6
	40	80.2		40	29.6
	50	79.0		50	29.0
	100	79.0		100	29.0
	200	79.0		200	28.4
	500	78.4		500	28.0
Silica.....	0	100.0	Ammonium.....	0	100.0
	10	44.2		10	100.0
	20	30.3		20	100.0
	30	22.2		30	100.0
	40	18.1		40	100.0
	50	14.4		50	100.0
	100	7.2		100	100.0
	200	2.8		200	100.0
	500	0.8		500	106.3

Aluminum, iron, and silica seriously interfere with strontium emission. Increasing concentrations of these ions cause a continuous decrease in emission intensity. Mitchell and Robertson (1936) state that aluminum extracts energy from the flame so that insufficient energy is available for excitation of the strontium atom. According to Hultdt (1946) and Servigne and Montgareuil (1954), aluminate and ferrate complexes of strontium are responsible for the marked decrease in the emission intensity. These authors attribute the effect to the very high decomposition temperatures of these refractory compounds that preclude excitation of the strontium. Although organic solvents are known to enhance the emission intensity of some elements, the

ethyl alcohol produced by the hydrolysis of tetraethyl orthosilicate gave no interference.

Vallee (1954) presented experimental evidence indicating that cationic interferences are caused by the superposition of monochromatic emission of cations upon heterochromatic background emission. He found that the heterochromatic background increased directly with the concentration of the radiating species.

Sulfate and phosphate sharply decrease the emission intensity of strontium to concentration ratios of sulfate-to-strontium and phosphate-to-strontium of as much as 3 to 1 and 1 to 1 respectively. At greater concentration ratios, no further decrease of the strontium emission was observed. Baker and Johnson (1954) postulate that the formation of partially dehydrated pyrosulfate or pyrophosphate in the flame reduces the energy of the flame and therefore prevents excitation of the strontium. Margoshes and Vallee (1956) report that because of the formation of strontium sulfate or phosphate, which have high melting and boiling points, the strontium salt is not dissociated in the flame and hence is not excited. Fukushima (1959) has shown that sulfate and phosphate interference is the result of a shift in equilibrium in the flame.

Fortunately, aluminum, iron, and phosphate are normally present in natural waters in amounts ranging from less than one to a few parts per million (Hem, 1959) and hence at these concentrations do not seriously interfere in the flame-photometric determination of strontium. In order to eliminate or reduce the interference of the other cations and anions tested, a radiation buffer was added to samples and standards. Skougstad (1957), showed that the addition of 1.0 g of potassium chloride and 0.5 g of ammonium citrate per 100 ml of solution eliminated the depressive effect of as much as 1,000 ppm of sulfate and 460 ppm of sodium. As shown in figure 3, the enhancement from sodium, potassium, and calcium reaches a plateau at about 200 ppm concentration, thus the addition of 10,000 ppm of radiation buffer to each sample and standard compensates for the effect of these ions in the water.

The effect of pH on the emission of strontium was also studied. Five series of solutions containing 1, 3, 5, 7, and 10 ppm of strontium and a radiation buffer (1.0 g of potassium chloride and 0.5 g of ammonium citrate per 100 ml) were prepared. Such a solution has a pH of approximately 5. The pH of four of the series was adjusted with hydrochloric acid or ammonium hydroxide, to 1.0, 3.0, 7.0, and 9.0 and the net emission intensity of each series measured. The maximum net intensities were obtained at pH values between 4 and 7 (fig. 4).

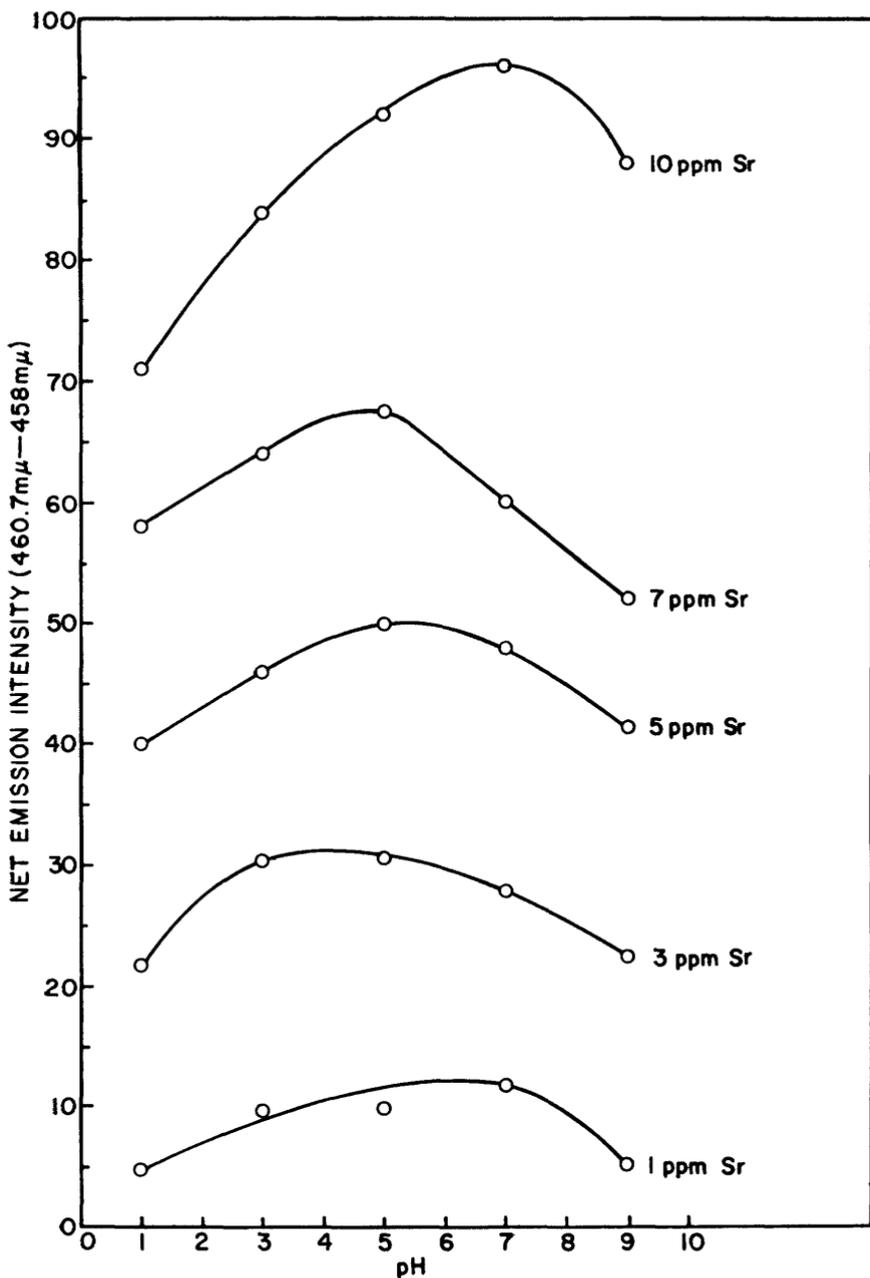


FIGURE 4.—Effect of pH on the emission intensity of strontium.

## ANALYTICAL PROCEDURE

## FLAME-PHOTOMETRIC METHOD

The flame-photometric method used for the determination of strontium in natural water is practically that described by Skougstad (1957). The method has been modified by adding the radiation buffer as a solution rather than as a solid, thus, eliminating the tedious weighing of the potassium chloride and ammonium citrate. Also, adjustment of the pH to the phenolphthalein end point has been eliminated. The emission intensity measured at the 460.7- $m\mu$  strontium line is corrected for superimposed background radiation by subtracting the emission intensity measured at 458  $m\mu$ .

This method may be applied to the determination of strontium at concentrations of from 0.2 to 10 ppm. Higher concentrations of strontium may be determined if the sample is diluted.

The procedure as adopted, is described below:

**Reagents used**

Use demineralized distilled water for the preparation of all solutions and chemicals of reagent (or, if available, spectroscopically pure) grade.

*Strontium stock solution:* 1,000 ppm. Dissolve exactly 1.6848 g of strontium carbonate, previously dried at 105 °C for 1 hour, in a minimal amount of dilute hydrochloric acid and dilute to 1 l. Store in a polyethylene bottle.

*Radiation buffer:* Dissolve 50.0 g of potassium chloride and 25.0 g of ammonium citrate (dibasic) in water and dilute to 500 ml. This solution will keep for about 2 months.

**Preparation of samples**

Prepare a series of standard strontium solutions, containing 1.0, 3.0, 5.0, 7.0, and 10.0 ppm strontium by adding aliquots of the strontium stock solution to 100-ml volumetric flasks that contain 10.0 ml of the radiation buffer. Dilute to the mark and mix thoroughly. Prepare a blank (0.0 ppm Sr) by diluting 10 ml of the radiation buffer to 100 ml.

Transfer a 50-ml aliquot of the unknown to a 100-ml volumetric flask, add 10 ml of the radiation buffer, and dilute the solution to 100 ml. Filter if the unknown contains any suspended matter prior to preparation for measurement, to prevent clogging the capillary of the atomizer burner.

**Measurement of strontium**

Use a Beckman DU spectrophotometer equipped with a flame attachment and a photomultiplier for all measurements and operate as follows:

Slit width: 0.01 mm

Sensitivity: 1 to 1½ turns from full counterclockwise

Selector: 0.1

Photomultiplier tube: full sensitivity, zero suppression off

Oxygen pressure: 11.0 psi } Gas pressures vary according to manufacturer's rec-  
Acetylene pressure: 0.5 psi } ommendation for the atomizer burner used.

Strontium line wavelength: 460.7  $m\mu$

Background wavelength: 458  $m\mu$

Because of the very narrow slit width used, a critical adjustment of the wavelength is necessary. With the shutter open and the transmission scale set at zero, adjust the dark current control to obtain a null point reading with the

blank (0.0 ppm) strontium standard. Then adjust the sensitivity control for 100 percent transmission with 10.0 ppm of strontium. Make readings for the 1.0, 3.0, 5.0, and 7.0 ppm standards and the correct readings for background by subtracting the readings taken at 458  $m\mu$  for each standard. The calibration data yield a straight line over the 0 ppm to 10.0 ppm strontium range (fig. 5).

Measure the net emission intensity of the unknown solutions, prepared as described above, and determine the strontium content from the calibration curve.

#### Calculations

Determine the strontium concentration in the sample from the calibration curve obtained from known amounts of strontium.

$$\text{Parts per million Sr} = \frac{1}{\text{density}} \times \text{parts per million Sr in sample} \times \text{dilution factor}$$

Report strontium concentrations of less than 1.0 ppm to the nearest 0.1 ppm, more than 1.0 ppm to two significant figures only.

#### ION-EXCHANGE METHOD

Strontium in water may be detected by the flame-photometric method described above in concentrations as low as 0.2 ppm without concentration of the samples prior to atomization in the flame. However, recent data (Skougstad and Horr, 1960) from a selected group of surface and ground waters show that the strontium content of a majority of these samples is below the detection limit for direct flame photometry. Because the flame-photometric method is not sensitive for less than 0.2 ppm strontium, it is necessary to increase the strontium concentration at least tenfold in a sample containing strontium in the range of 0.02 to 0.2 ppm.

Concentration of strontium in water by precipitation reactions is cumbersome owing to the large volume of water required to obtain sufficient strontium for easy recovery. Concentration by evaporation is time consuming and also may cause precipitation of salts that would clog the atomizer burner. These methods of concentration are unsuited for the analyses of a large number of samples.

In the analysis of natural water, ion-exchange chromatography is used primarily for the concentration of trace amounts of elements in solution or for the removal of ions that interfere in a particular analytical method. Concentration of trace elements in solution by ion-exchange chromatography has been described by Cranston and Thompson (1956), Riches (1946, 1947), and Egner and others (1949). Tomkins and others (1947), Stanley and Kruger (1956), and Milton and Grummitt (1957) have described methods for the separation of strontium from the alkali metals and the other alkaline-earth metals. However, it is difficult to make a precise separation of strontium from these cations. Fortunately, a complete separation of strontium from other cations is unnecessary as their effect in the flame-photometric determination of strontium is compensated by subtraction of the background radiation.

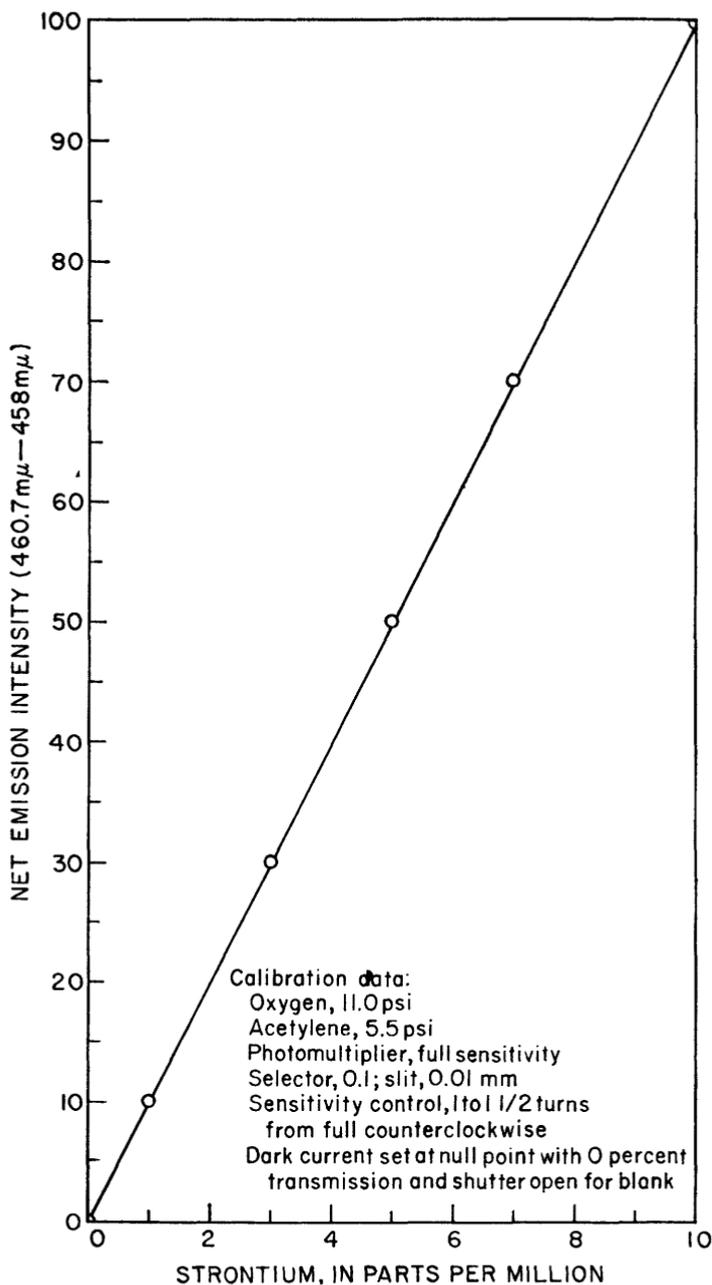


FIGURE 5.—Typical calibration curve.

Strontium and other cations in water are concentrated from a large volume of a relatively dilute solution by absorption on a cation-exchange resin followed by elution with a small volume of concentrated eluate. Satisfactory results were obtained by absorption on a resin in the hydrogen form and elution with hydrochloric acid, but this procedure was abandoned because of the objection to atomizing large quantities of the acid during the measurement of the strontium content of the eluate.

Ammonium acetate and ammonium acetate-acetic acid mixtures as eluates for strontium were investigated. Strontium was absorbed on a cation-exchange resin in the ammonium form and the following solutions tested for their efficiency as eluate for strontium (1) 1*M* ammonium acetate, (2) 1*M* ammonium acetate-1*M* acetic acid, and (3) 2*M* ammonium acetate-1*M* acetic acid. Successive 5-milliliter fractions of the eluate were collected and the strontium content of each measured by flame photometry.

Of the three eluates tested, the 2*M* ammonium acetate-1*M* acetic acid gave the best results (fig. 6). Although the 2*M* ammonium acetate-1*M* acetic acid curve shows some tailing, this causes no serious error in the determination of strontium. A solution of 4*M* ammonium acetate-2*M* acetic acid also was tried as an eluate, but proved useless because of the extremely slow aspiration rate in the atomizer burner.

Figure 7 shows the results obtained with 2*M* ammonium acetate at a pH of 8.5 and 7.3 as compared to the 2*M* ammonium acetate-1*M* acetic acid at a pH of 5.4. Better results were obtained with the latter. The elution curves for strontium and calcium, using 2*M* ammonium acetate-1*M* acetic acid as the eluate are shown in figure 8.

#### Analytical procedure

Condition Amberlite IR-120 cation-exchange resin to remove impurities and grade to 32- to 42-mesh particle size. Place ten milliliters of this resin in a chromatographic column, converted to the ammonium form, and rinse. Pass a 500-ml sample through the column and rinse with distilled water. Elute the strontium and other absorbed cations with 50 ml of ammonium acetate-acetic acid solution, thus making a tenfold concentration of these cations to that of the original sample. Determine the strontium content of the eluate by the flame-photometric procedure previously described.

#### Reagents

Elutant: Dissolve 154.2 g of reagent grade ammonium acetate in water, add 57.8 ml of glacial acetic acid and dilute to approximately 800 ml. Adjust the pH to 5.4 with ammonium hydroxide and dilute to 1 l. Filter the solution before use.

Recharge solution: 5-percent ammonium chloride.

Exchange resin: Amberlite IR-120 prepared as described below.

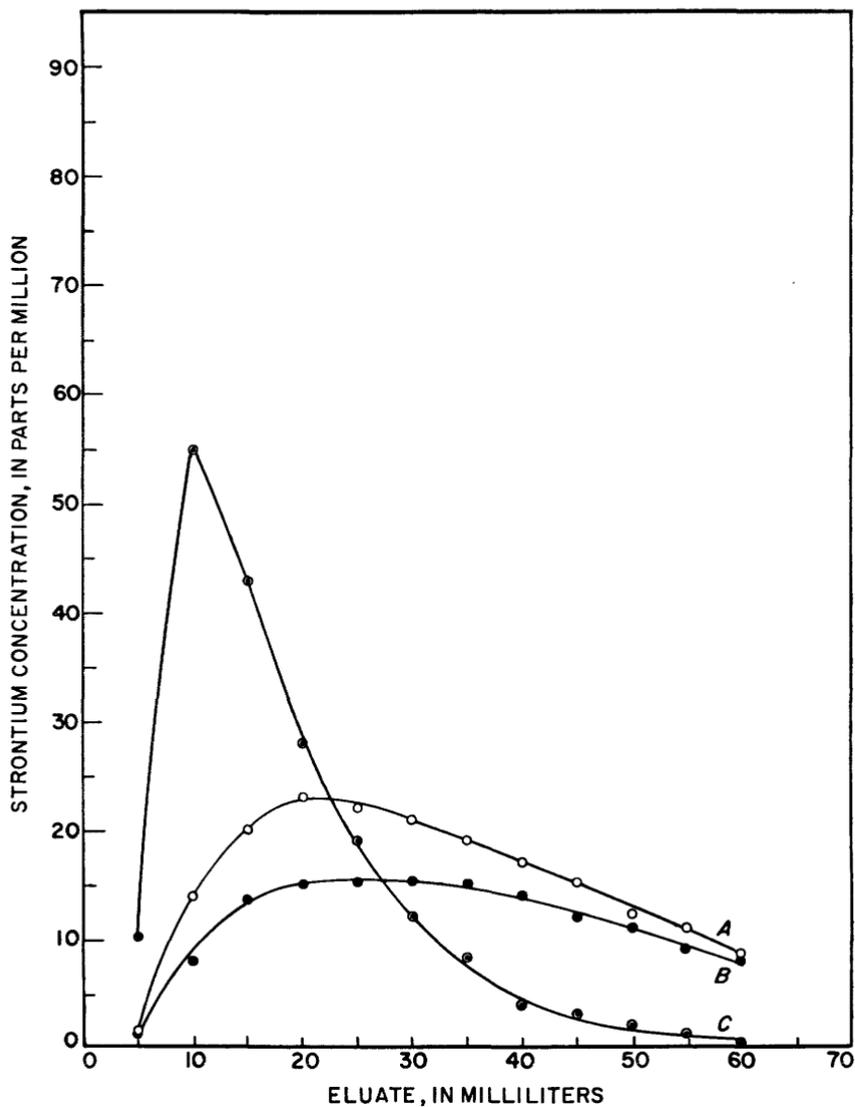


FIGURE 6.—Elution of strontium with (A) 1M  $\text{NH}_4\text{OAc}$ -1M  $\text{HOAc}$ , pH 4.8; (B) 1M  $\text{NH}_4\text{OAc}$ , pH 7.0; (C) 2M  $\text{NH}_4\text{OAc}$ -1M  $\text{HOAc}$ , pH 5.4.

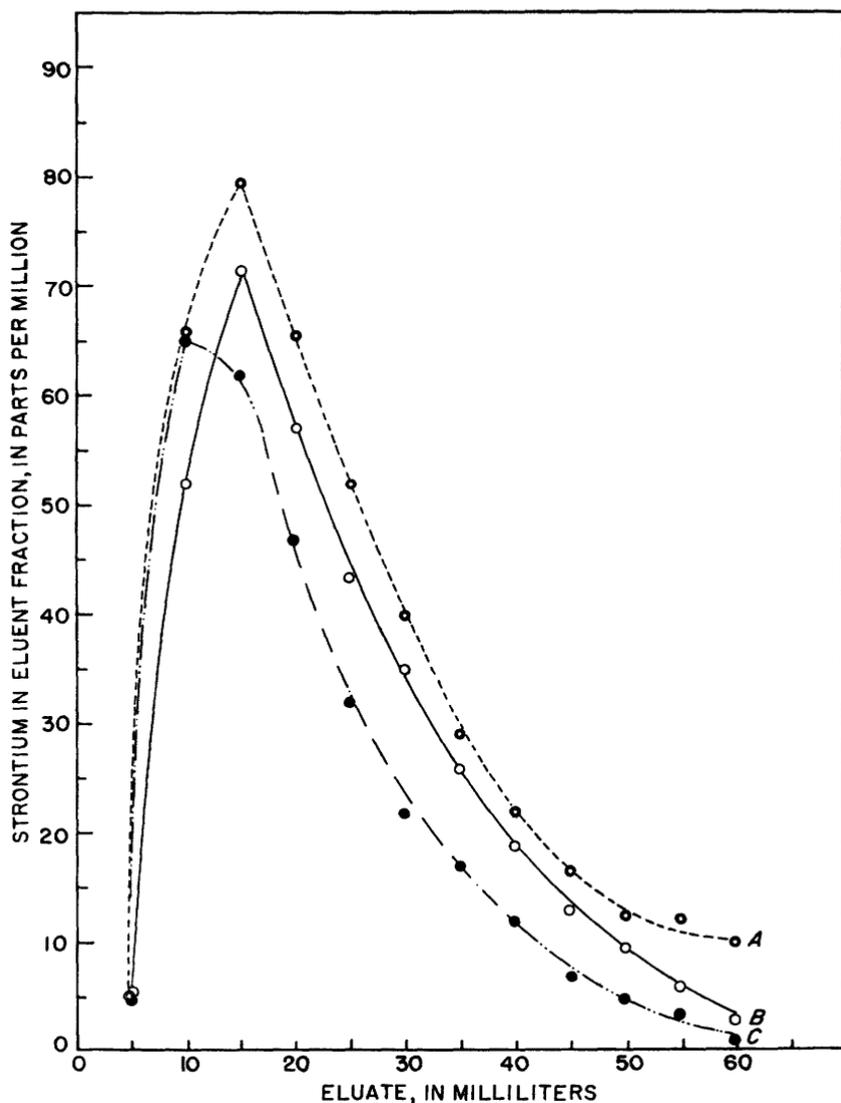


FIGURE 7.—Elution of strontium with (A)  $2M$   $NH_4OAc$  at pH 7.3; (B)  $2M$   $NH_4OAc$ , pH 7.0; (C)  $2M$   $NH_4OAc$   $1M$   $HOAc$  at pH 5.4.

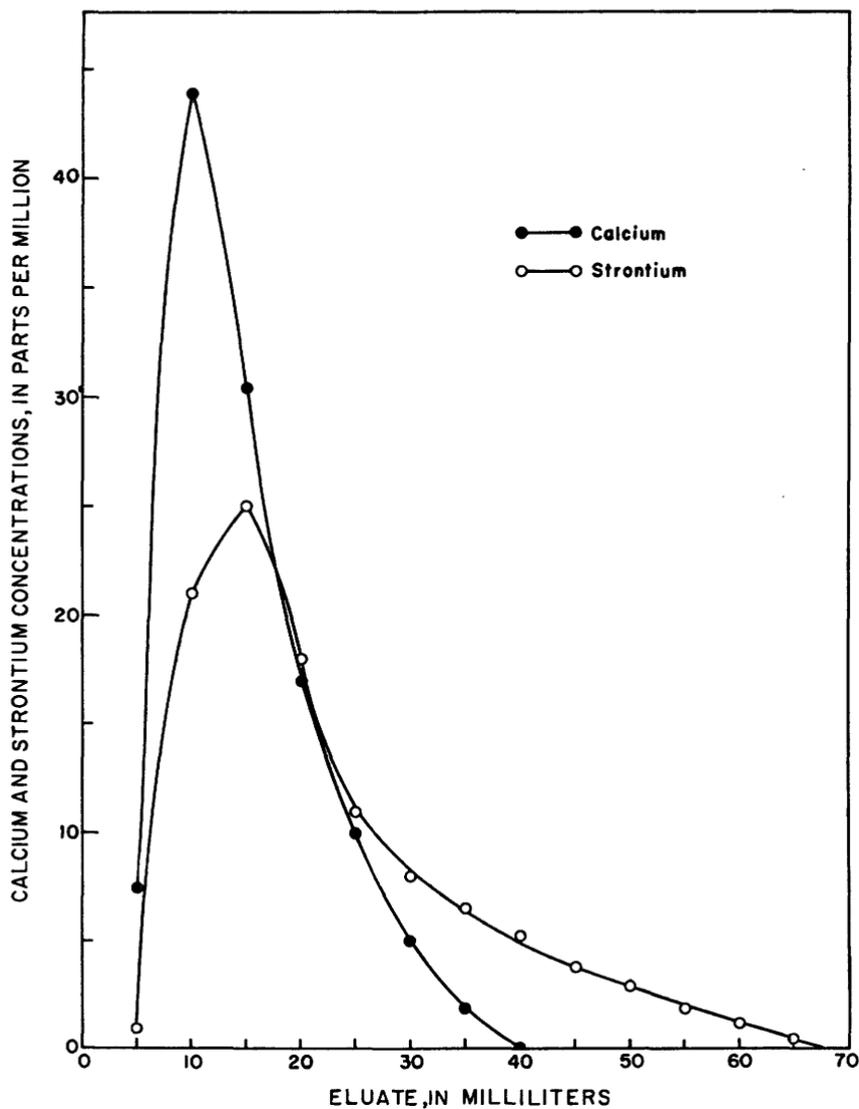


FIGURE 8.—Elution curves for calcium and strontium using  $2M$   $NH_4OAc$ - $1M$   $HOAc$  at pH 5.4 as eluate.

#### Preparation of resin

Condition Amberlite IR-120 cation-exchange resin, which was found to be satisfactory, before use to remove traces of iron and other impurities. Place the resin in a separatory funnel and shake with 6*N* sodium hydroxide for about 10 minutes. Decant excess sodium hydroxide, and wash the resin thoroughly with distilled water by allowing the water to flow slowly upward through the stem of the funnel. Repeat the procedure with 6*N* hydrochloric acid to convert the resin to the hydrogen form. Wash the resin with distilled water until the pH of the influent and effluent is the same.

Grade the resin for particle size by wet sieving through a nested set of 20- 32- 42- (or 20- 35- 45-) mesh sieves in the following manner: Place the conditioned resin on the top (20-mesh) sieve and lower the assembly gently into a beaker filled with distilled water. Raise the nested sieves quickly allowing the water to drain into the beaker. Continue to alternate lowering and raising of the sieves until sufficient resin of 32- to 42- (or 35- to 45-) mesh particle size is obtained for packing the column.

#### Preparation of ion-exchange column

The size of the ion-exchange column depends upon the exchange capacity of the resin and the maximum cation concentration of the waters being examined. Amberlite IR-120 has a cation-exchange capacity of 1.9 milliequivalents per milliliter of wet resin; thus, a column containing 10 ml of resin is sufficient to completely exchange the cations in 500 ml of water containing as much as 38 equivalents per million of cations.

Fill a chromatographic tube (fig. 9) with distilled water, add 10 ml of the graded resin as a slurry, and allow to settle. Insure uniform packing of the column to avoid channeling and air spaces within the column, which greatly reduces its efficiency. After a uniformly packed column has been obtained drain the water to the top of the resin bed and pass approximately 100 ml of a 5-percent ammonium chloride solution through the column. Rinse the column with 100 ml of distilled water. The resin is now in the ammonium form and ready for use. The chromatographic tube, shown in figure 9, was constructed to require minimum attention during the adsorption cycle. The resin bed will not become completely drained during operation, as may occur if a buret is used for the chromatographic column.

#### Concentration of strontium

Filter samples that contain suspended material to prevent clogging of the column. Pass measured volume of the water sample—usually 500 ml, whose total cation concentration does not exceed the exchange capacity of the resin column—through the column at a rate of 1 to 1.5 ml per minute. After the sample has passed through the column, rinse the column with 50 ml of distilled water to remove traces of anions, and discard the effluent.

Elute the strontium, together with other cations, from the column with a solution of 2*M* ammonium-acetate-1*M* acetic acid adjusted to a pH of 5.4 with ammonium hydroxide.

Collect exactly 50 ml of the eluate in a volumetric flask. Rinse the column with 100 ml of distilled water after elution and it is then ready for the next analysis.

#### Measurement of strontium

Prepare standard solutions by passing 50 ml each of standards containing 0.0, 1.0, 3.0, 5.0, 7.0, and 10.0 parts per million strontium through the exchange column and elute with 50 ml of the 2*M* ammonium-acetate-1*M* acetic acid solution. Use results from flame-photometric determinations to prepare a calibration curve and

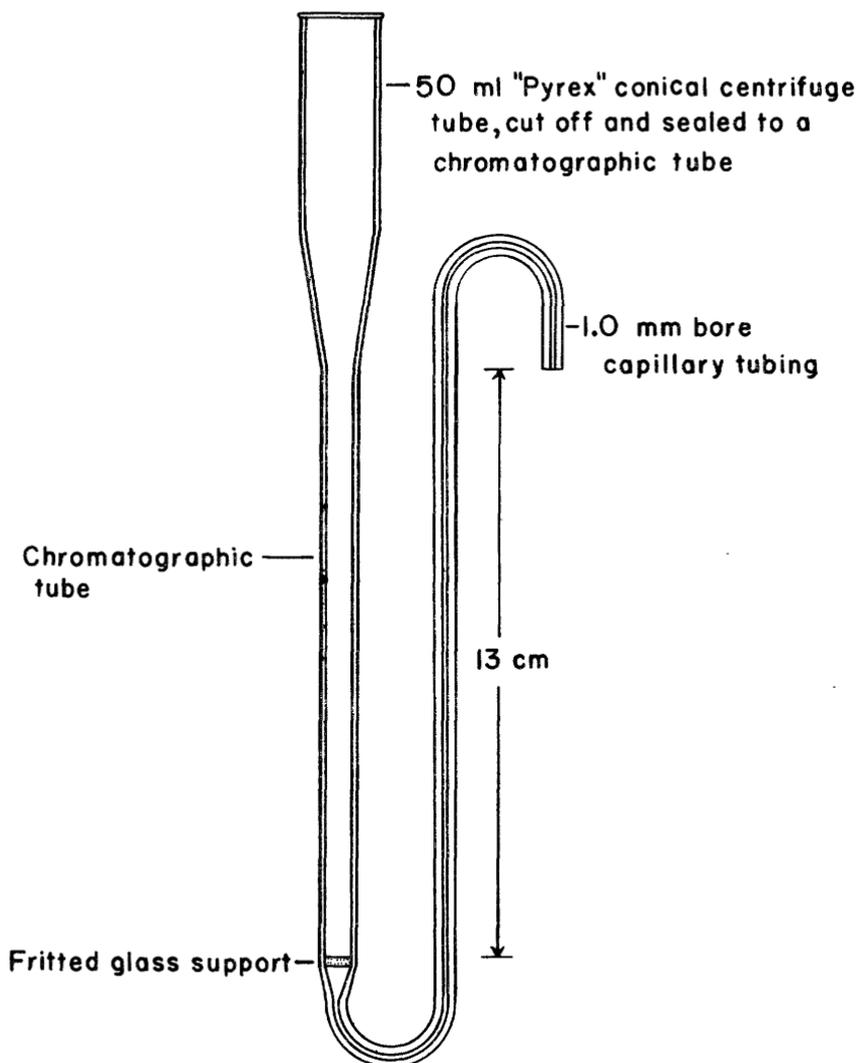


FIGURE 9.—Ion-exchange column.

to make the quantitative determination of strontium in the eluate from the unknown sample.

#### Calculations

Determine the strontium concentration in the eluate of an unknown sample from the calibration curve of standards containing known amounts of strontium.

$$\text{Part per million Sr} = \frac{1}{\text{density}} \times \frac{\text{parts per million Sr in eluate}}{\text{concentration factor}}$$

Report strontium concentrations of less than 1.0 ppm to nearest 0.01 ppm and concentrations greater than 1.0 ppm to two significant figures only.

RESULTS AND DISCUSSION

A comparison of results obtained on routine samples by the flame-photometric, the ion-exchange flame-photometric and the spectrograph (Skougstad, 1961) methods is shown in table 3. The values ob-

TABLE 3.—Comparison of results obtained by the flame-photometric, ion-exchange flame-photometric, and spectrographic methods

[Results in parts per million]

Sample	Strontium found by indicated method:			Sample	Strontium found by indicated method:		
	Flame-photometric	Ion-exchange flame-photometric	Spectrographic		Flame-photometric	Ion-exchange flame-photometric	Spectrographic
2640	<0.2	0.14	0.14	2917	<0.2	0.16	0.13
2723	.8		.74	2953	.4		.44
2785	.4	.47	.42	2958	.2		.19
2802	.4	.37	.47	3492		.21	.18
2874	.8		1.0	3558		.08	.06
2876	.8	.85	.8				

tained by the flame-photometric and ion-exchange flame-photometric methods agree within 13 percent of the spectrographic results. The variation between the flame-photometric and ion-exchange flame-photometric methods was 10 percent.

Strontium was added to tap water and analyzed by the flame-photometric method. The results, table 4, show an average deviation of 0.10 ppm from the amount of strontium added. The recovery varied from 80 to 104 percent.

The results of a similar study for the ion-exchange flame-photometric method is shown in table 5. A synthetic water, containing one-tenth the average concentration of the major cations and anions found in sea water, was used to prepare three 500-milliliter samples containing known amounts of strontium. These samples were then concentrated by ion-exchange and analyzed by flame photometry.

TABLE 4.—Recovery of strontium, in parts per million, added to tap water

[Analysis by the flame-photometric procedure]

Sample	Sr added	Sr found	Error	Sample	Sr added	Sr found	Error	Sample	Sr added	Sr found	Error
1a	1.00	0.8	-0.2	2a	1.35	1.4	+0.05	3a	4.20	4.1	-0.1
b	1.00	.9	-1	b	1.35	1.4	.05	b	4.20	4.0	-.2
c	1.00	.9	-1	c	1.35	1.4	.05	c	4.20	4.0	-.2
d	1.00	1.0	0	d	1.35	1.4	.05	d	4.20	4.1	-.1
e	1.00	.9	-1	e	1.35	1.4	.05	e	4.20	4.0	-.2
Average error			-.10	Average error			+0.05	Average error			-.16

TABLE 5.—*Recovery of strontium added to a synthetic water*<sup>1</sup>

[Analysis by ion-exchange flame photometry. Results in parts per million]

Sample	Sr added	Sr found	Error
A-----	0.08	0.09	0.01
B-----	.14	.14	.00
C-----	.18	.18	.00
D-----	.00	.03	.00

<sup>1</sup> This synthetic water contains, per liter, the following:

	Grams		Grams
NaCl-----	4.696	CaCl <sub>2</sub> -----	0.220
MgCl <sub>2</sub> .6 H <sub>2</sub> O-----	2.130	KCl-----	.146
Na <sub>2</sub> SO <sub>4</sub> .10 H <sub>2</sub> O-----	1.780	NaHCO <sub>3</sub> -----	.038

<sup>2</sup> The synthetic water contained 0.03 ppm Sr from reagents used in preparation. This blank was subtracted from results of A, B, and C.

A recovery of from 100 to 112 percent of the added strontium was obtained.

The flame-photometric method is useful for determining strontium in concentrations as low as 0.2 ppm with an accuracy of 10 percent. A tenfold concentration of strontium in water is accomplished by the ion-exchange method by passing the sample through the ion-exchange column and eluting with ammonium acetate-acetic acid solution. Strontium may then be determined at concentrations as low as 0.2 ppm in the ammonium acetate-acetic acid eluant giving a determination limit of 0.02 ppm of strontium in the original sample. The limit of accuracy is 10 percent.

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